

Supplementary Information

An unprecedented 3D 8-connected pure inorganic framework based on nanosized {[Na₁₂PO₁₆H₂₄]C[P₄Mo₆O₃₁H₆]₄}¹⁵⁻ clusters and zinc cations

Dong-Ying Du, Jun-Sheng Qin, Yang-Guang Li, Ya-Qian Lan*, Xin-Long Wang, Kui-Zhan Shao,
Zhong-Min Su* and En-Bo Wang

*Institute of Functional Material Chemistry, Key Lab of Polyoxometalate Science of Ministry of
Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, P. R. China.
Fax: +86-431-85684009; Tel: +86-431-85099108. E-mail: zmsu@nenu.edu.cn.*

1. Materials and Measurements

All the chemicals were obtained from commercial sources, and were used without further purification. Elemental analyses (C, H and N) were measured on a Perkin-Elmer 2400 CHN elemental analyzer; Mo, Zn and P were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. IR spectrum was performed in the range 4000-400 cm^{-1} using KBr pellets on an Alpha Centaur FT/IR spectrophotometer. Powder X-ray diffraction measurement was recorded radiation ranging from 5 to 50° at room temperature on a Siemens D5005 diffractometer with Cu-K α ($\lambda = 1.5418 \text{ \AA}$). Diffuse reflectivity was measured from 200 to 2000 nm using barium sulfate (BaSO_4) as a standard with 100% reflectance on a Varian Cary 500 UV-Vis spectrophotometer. Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 1000 °C under nitrogen at the heating rate of 5 °C \cdot min $^{-1}$. A conventional three-electrode system was employed to study the cyclic voltammetric behavior and electrocatalysis toward H_2O_2 . The glass carbon electrode was used as a working electrode; saturated calomel electrode as a reference electrode; Pt coil as a counter electrode, and the 0.1 mol \cdot L $^{-1}$ $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH = 3) solution was used as electrolyte.

2. Synthesis

Synthesis of **1**: A mixture of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (1.5 g, 6.20 mmol) and H_3PO_3 (0.12 g, 1.46 mmol) in 10 mL of water was adjusted the pH to 4 ~ 5 and stirred for 20 min. And then ZnCl_2 (0.10 g, 0.73 mmol) were added to the mixture, stirring for another 20 min, and then transferred and sealed in a 23 mL Teflonlined stainless steel container, which was heated at 170 °C for 5 days, and then cooled to room temperature at 10 °C \cdot min $^{-1}$, deep red octahedral crystals suitable for X-ray crystallography were obtained, washed with distilled water and then air-dried to give **1** in 62% yield (based on P). Elemental analysis: Anal. Calc.: H 2.03; Mo 35.37; Zn 6.03; P 8.09. Found: H 2.06; Mo 35.42; Zn 5.96; P 8.07%.

3. Crystallographic data for **1**

Crystallographic data for **1** ($\text{H}_{131}\text{Mo}_{24}\text{Na}_{12}\text{O}_{180}\text{P}_{17}\text{Zn}_6$), $M_r = 6509.20$, cubic, space group $Fd-3c$, $a = 40.5056(14) \text{ \AA}$, $V = 66458(4) \text{ \AA}^3$, $Z = 16$, $\mu = 2.924 \text{ mm}^{-1}$, $D_c = 2.602 \text{ g cm}^{-3}$, $F(000) = 50336$, 2450 unique ($R_{\text{int}} = 0.0807$), $R_1 = 0.0580$, $wR_2 = 0.1620$ ($I > 2\sigma(I)$), $GOF = 1.099$, $T = 293(2) \text{ K}$. Max./min. residual electron density 1.855 and $-1.979 \text{ e \AA}^{-3}$. A total of 76458 data were measured in the range $1.42^\circ < \theta < 25.00^\circ$. The data were corrected for absorption by the multi-scan. The H atoms have not been located, but were included into the formula directly. CCDC 796531.

4. the redox titration experiment

(1) Preparation of KMnO_4 solution (its concentration is approximately $0.01 \text{ mol}\cdot\text{L}^{-1}$)

Note: The solution should be boiled for 2 hour in order to deoxidize, and then stored in a brown bottle.

(2) Calibration of the concentration of KMnO_4 solution with $\text{Na}_2\text{C}_2\text{O}_4$

Note: (i) addition of 15 drops H_2SO_4 ($18 \text{ mol}\cdot\text{L}^{-1}$) to each simple solution; (ii) 70°C water bath.

(3) Determination of the oxidation state of Mo

The titration method is similar with (2); the only difference is that the sample is the mixture of a certain amount of compound **1** and $\text{Na}_2\text{C}_2\text{O}_4$.

Conclusion: The redox titration of compound **1** was carried out in acidic solutions against standardized KMnO_4 solution. The results showed that the oxidation state of Mo is +5 in **1**.

5. the detail description of coordinated environment of zinc ions

Every two $\{\text{ZnO}_4\}$ tetrahedra share one oxygen atom (O9) and bridge six distinct $\{\text{P}_4\text{Mo}_6\}$ moieties from two tetrameric clusters to give a $\{\text{Zn}_2\text{O}_7\}$ unit, which can be viewed as two 'bowls' connecting in the bottom-to-bottom fashion (Fig. S1a, ESI†). Each octahedral divalent zinc cation connects two $\{\text{P}_4\text{Mo}_6\}$ fragments from two tetrameric clusters generating a sandwich-shaped $[\text{Zn}(\text{P}_4\text{Mo}_6)_2]$ dimer, which can be viewed as two 'plates' connecting in the back-to-back mode (Fig. S1b, ESI†). The most fascinating and peculiar structural feature of **1** is that not only $\{\text{ZnO}_6\}$ units but $\{\text{Zn}_2\text{O}_7\}$ units can be considered to adopt the staggered conformation (Fig. S2, ESI†).

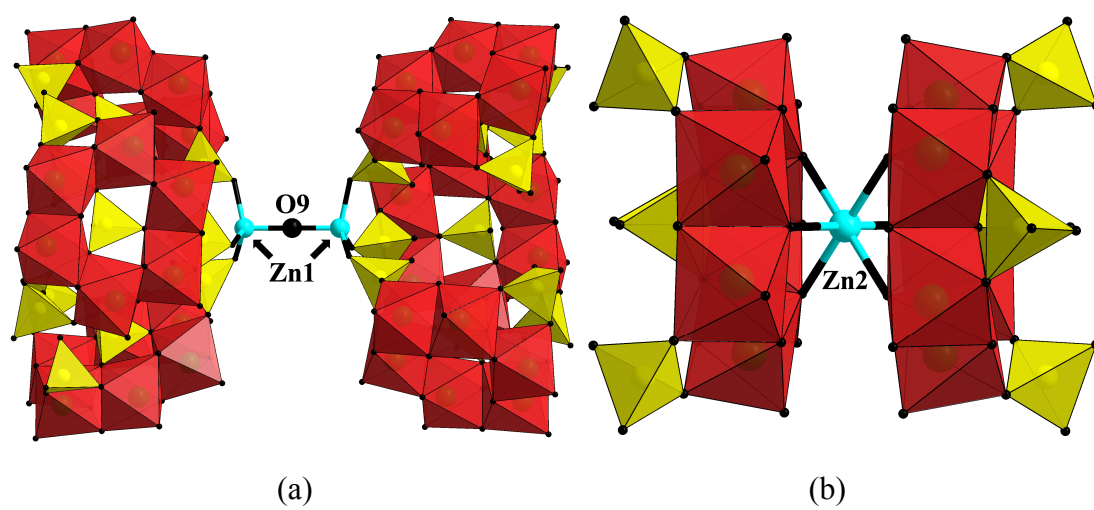


Fig. S1. View of connectivity modes of Zn1 (a) and Zn2 (b) centers.

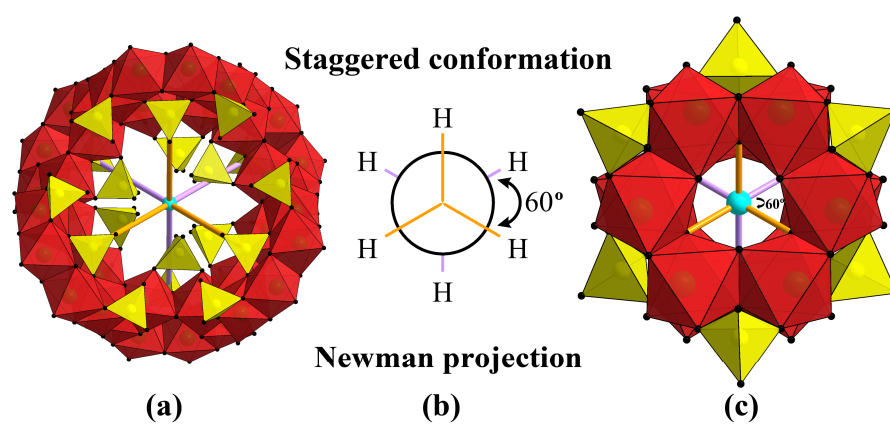


Fig. S2 Both Zn1 and Zn2 centers linked $\{P_4Mo_6\}$ units in *staggered* conformations.

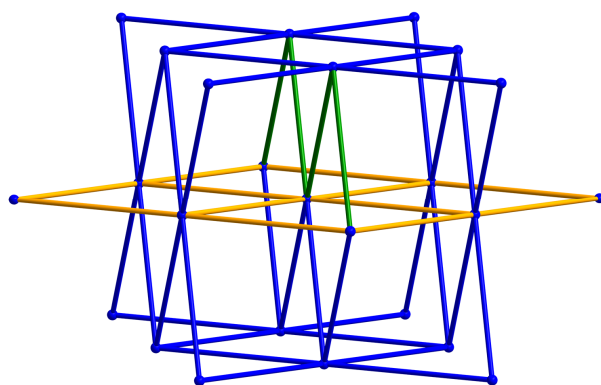


Fig. S3. Schematic representation of the eight-connected **bcu** topology in **1**

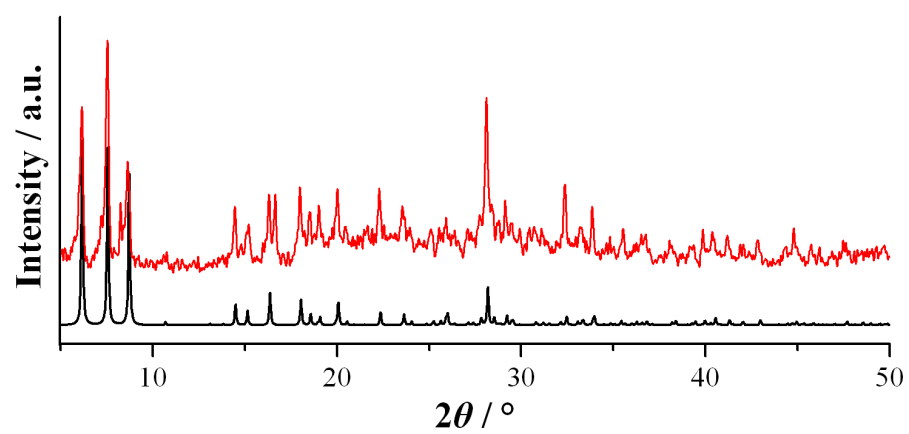


Fig. S4 The XRPD pattern (top) and simulated pattern (bottom) of **1**.

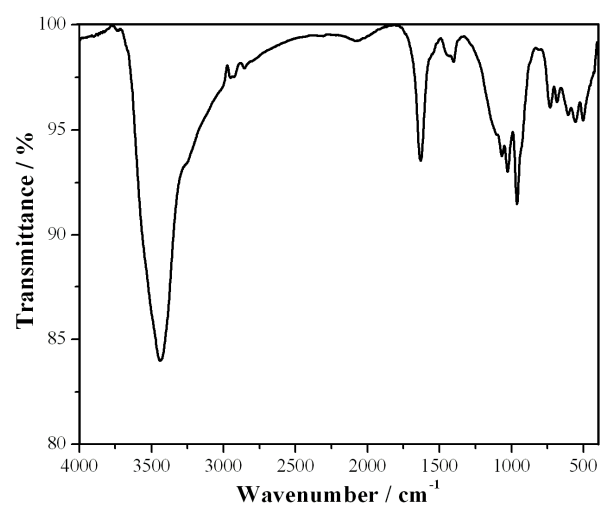


Fig. S5. The IR spectrum of **1** in KBr pellets from 4000 cm^{-1} to 400 cm^{-1} .

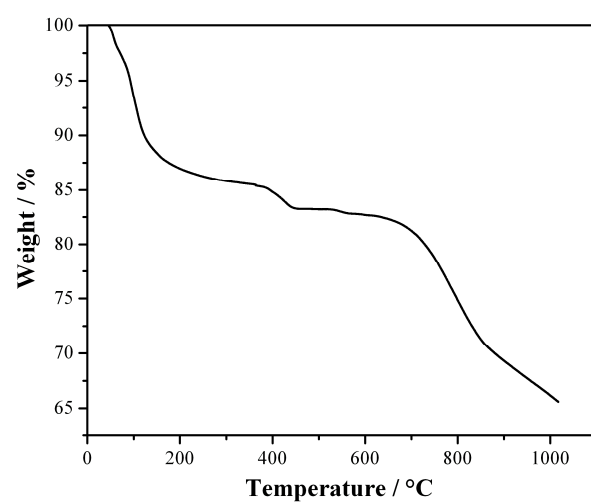


Fig. S6. The TGA curve of **1** measured under N_2 atmosphere from room temperature to 1000 $^{\circ}\text{C}$ at the

ating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

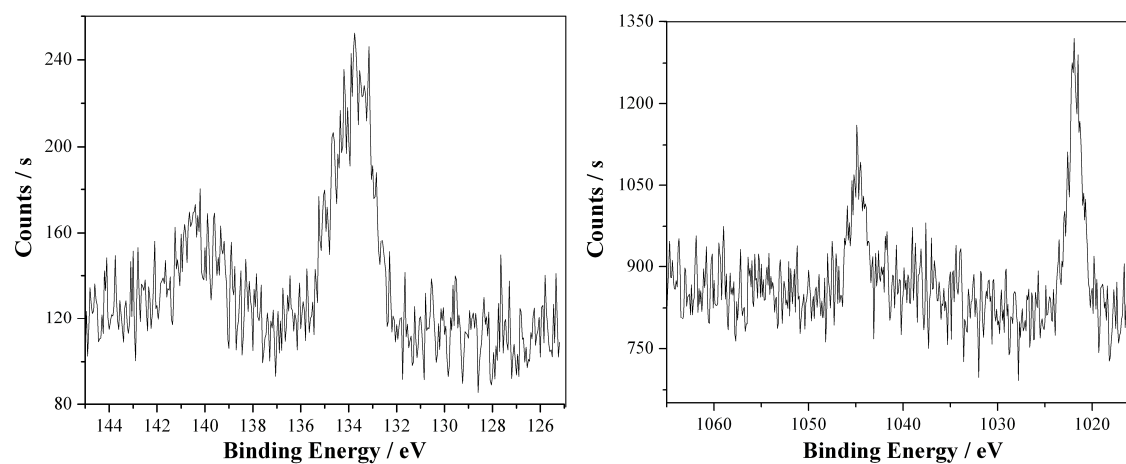


Fig. S7. The XPS spectra of compound **1**, (a) P and (b) Zn.

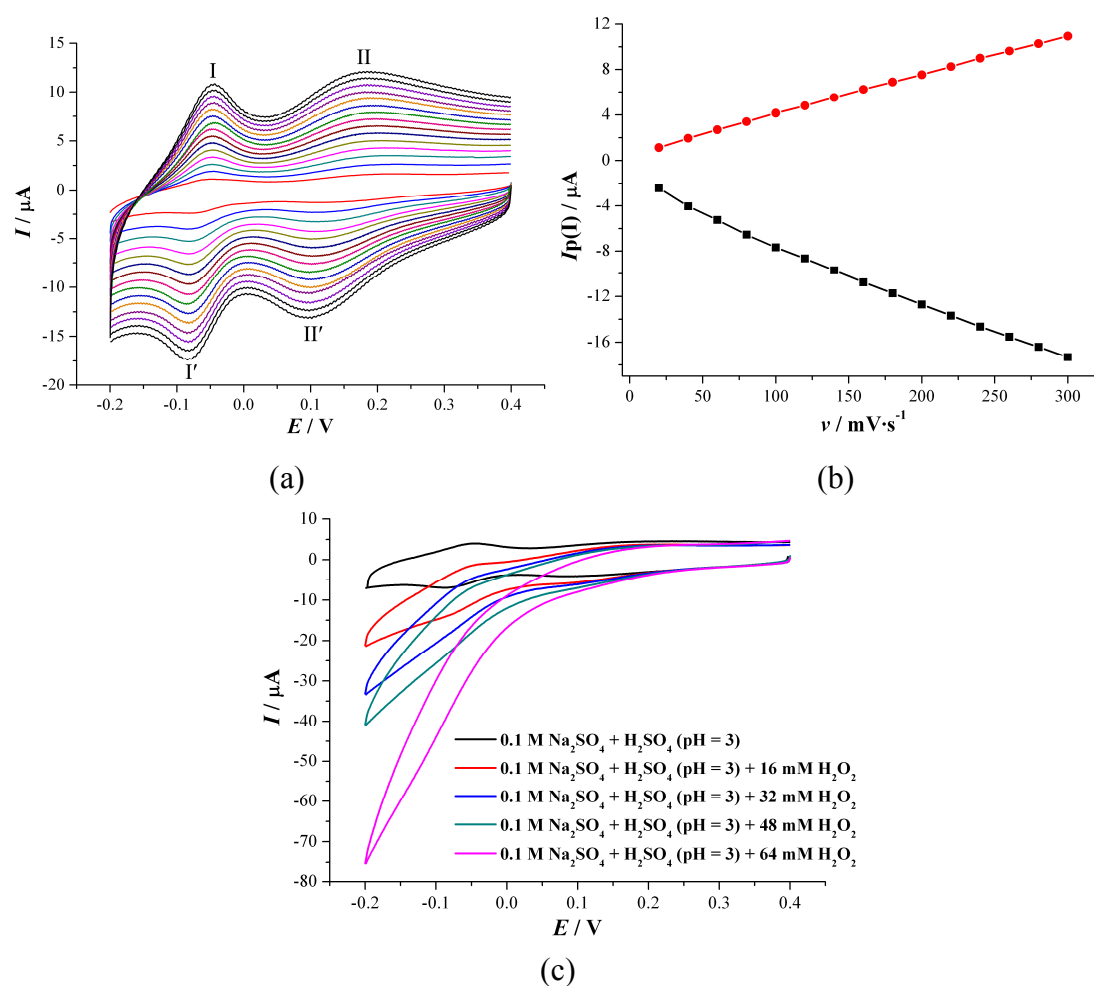


Fig. S8. (a) The cyclic voltammograms of **1** in $0.1\text{ mol}\cdot\text{L}^{-1}\text{ Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH = 3) at different scan rates (from inner to outer: 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 300 $\text{mV}\cdot\text{s}^{-1}$); (b) The plots of the anodic and the cathodic peak I-I' currents against scan rates for **1**-CPE; (c) Cyclic voltammograms of **1** in $0.1\text{ mol}\cdot\text{L}^{-1}\text{ Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH = 3) containing different

concentrations of H_2O_2 (at the scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$).

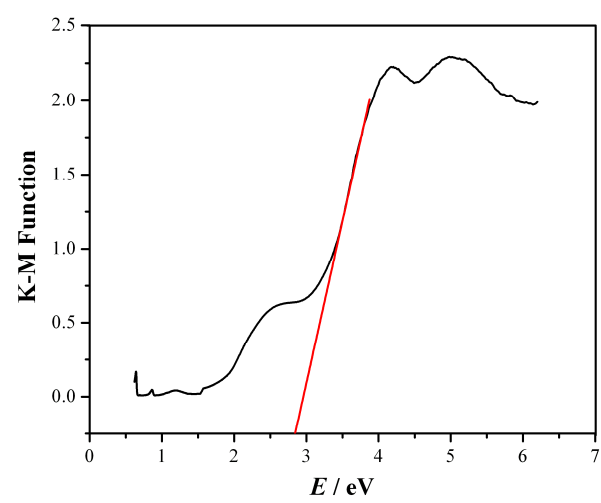


Fig. S9. Diffuse reflectance UV-Vis spectrum of K–M function versus E (eV) of compound **1**.